

EXHIBIT E

Reactive Hot Melt Adhesives

SpecialChem - Nov 21, 2002

Edward M. Petrie, Member of SpecialChem Technical Expert Team.

Introduction

Chemistry

Curing and Processing Properties

Equipment Requirements

Applications

Other Reactive Hot Melt Systems

Summary

Introduction

A reactive hot melt adhesive is any thermoplastic adhesive or sealant that can be applied at elevated temperatures as a liquid melt, cools to become a solid at room temperature, and then subsequently reacts to become a thermosetting polymer with enhanced physical properties. Hot melt adhesives can be made to be reactive in several ways.

Reactive hot melt adhesives have been available since the 1980s. Due to their thermoplastic nature during application, they have many of the desirable processing characteristics of conventional hot melts, such as no solvents present, no mixing requirements, and immediate green strength. Although conventional, nonreactive hot melt adhesives (e.g., ethylene vinyl acetate, polyalphaolefin, polyester, and polyamide) are widely used in many industrial applications, they have certain performance limitations, such as poor heat resistance, water or solvent permeation, and creep. These limitations generally prevent their use in many critical or structural bonding applications.

By being capable of curing to a thermosetting material, reactive hot melt adhesives eliminate or greatly reduce many of the performance problems associated with conventional hot melt adhesives. In addition, reactive hot melt adhesives have the ability to bond to many different substrates and, generally, have longer service life times. The advantages of these systems, however, do not come without some cost - generally a high material price and more difficult application processes. Table 1 summarizes the advantages and disadvantages in using reactive hot melt adhesives.

Advantages	Disadvantages
Lower application temperatures than conventional hot melts allow for reduced energy costs and lower safety concerns.	Higher material cost.
Low or no VOCs.	Full cure takes several days.
No mixing required (single component).	Open time may be short (seconds) depending on the substrate.
Immediate green strength and fast development of cohesive strength (crosslinking).	Moisture sensitivity could cause material to "set" in the applicator necessitating purging and cleaning process.
When compared to conventional hot melts:	
<ul style="list-style-type: none"> ● Improved high temperature resistance ● Enhanced moisture and solvent resistance ● Improved adhesion to the substrate ● Improved creep resistance ● Tough and flexible 	Special application equipment may be needed depending on the form and formulation of the product - to maintain moisture proof environment until application.
Significant freedom in formulation ability.	
Tensile strengths ranging from 2,000 psi (1,400 N/cm ²) to 3,500 psi (2,400 N/cm ²)	
Elongation at break from 290 to 750%	

Table 1: Advantages and Disadvantages of Hot Melt Polyurethane (HMPUR) Adhesives

By far, the most common reactive hot melt system is a polyurethane family of adhesives based upon moisture curing technology. There are also several other reactive hot melt adhesive systems based on non-polyurethane moisture curable polymers or on reactive UV curing processes. This paper concentrates primarily on the polyurethane reactive hot melts, sometimes known as HMPUR (hot melt polyurethane rubber) or "warm-melt" adhesives (to emphasize that these systems are applied at lower temperatures than conventional, non-reactive hot melts).

Chemistry



Reactive polyurethane hot melt adhesives are highly viscous or solid prepolymers with a low melting point. Reacting solid polyether or polyester polyol mixtures with an excess of diisocyanate produces the solid polyurethane prepolymer. The reaction of the isocyanate group (NCO) with an alcohol group (OH) on the polyol produces the urethane group as shown in Figure 1. The resulting product has a low number of free isocyanate groups depending on the final molecular weight and melt viscosity.

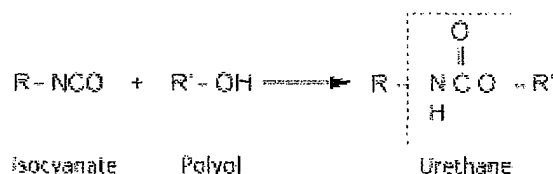


Figure 1: Reaction used in manufacturing a urethane prepolymer for use in reactive hot melt adhesives

The same general rules used in liquid polyurethane prepolymers applies to hot melt adhesives. For a given polyol system:

- higher NCO/OH ratios produce adhesives with lower melt viscosity, lower elongation at break, higher tensile modulus, and extended open times
- lower NCO/OH ratios with lower molecule weight polyether polyols produce thermoplastic characteristics with improved flexibility and toughness.

The prepolymer is then transferred as a melt from the reactor into a container and cools to form a solid product. Final product forms are bulk (drums and pails), slugs, cartridges, and granules. The container is tightly sealed to prevent exposure of the prepolymer to moist air. This is the adhesive product and form that are available to the end-user. There are several commercial sources of HMPUR adhesives including 3M (JetWeld), Reichhold (Ever-Lock), Franklin (ReacTITE and HiPURformer), Rohm and Haas (Mor-Melt), National Starch and Chemical, Seaco, and Jowat.

The solid prepolymers are capable of flowing at relatively low temperatures (85-140?) and wetting out the surface of the adherend like a conventional hot melt adhesive. The viscosity of the melt can be varied depending on specific requirements, but is generally in the range of 2,000 to 80,000 cps. These prepolymer melts provide a high degree of green strength and possess enough molecular weight to provide cohesive strength, flexibility, and adhesion to hold substrates together as a hot melt while the moisture curing mechanism progresses to provide crosslinking.

Once applied via a hot melt applicator, the residual non-reacted isocyanate groups react with ambient moisture to convert the polyurethane from a thermoplastic to a thermoset. The reaction of the isocyanate with water (Figure 2) forms the highly stable crosslinked polyurea structure that gives the cured polyurethane its high degree of performance. The moisture is available either from the substrate or from the ambient air.

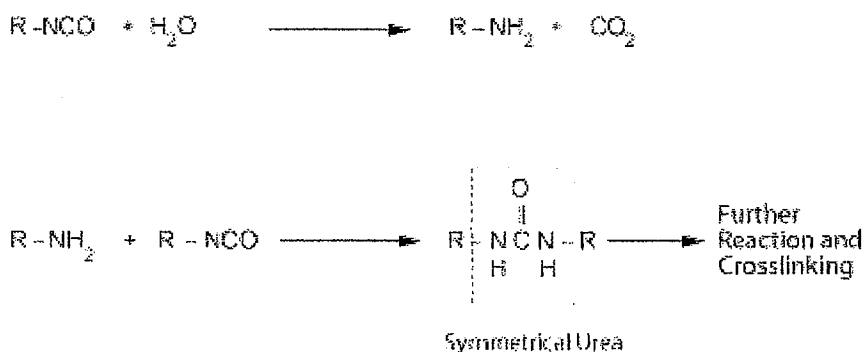


Figure 2: Reaction used in moisture curing polyurethane hot melt within the joint

The cross linking reaction takes several hours or even days to complete depending on the specific formulation, substrate, and relative humidity. This reaction can continue as long as moisture can enter into the material and there are available isocyanate groups. Several catalysts are used for reacting water with isocyanates in these formulations and accelerate the rate of cure. They include stannous octoate, dibutyl tin dilaurate, and triethylenediamine. The choice of catalyst depends, in part, on the stability of the reactive mixture at its temperature in the hot melt applicator.

In addition to the catalyst, specific properties can be built into the adhesive through formulation with a variety of polyols, isocyanates, and additives. The actual formulations are dictated by end-use requirements and cost. The type of polyol influences the physical properties of the cured as well as the uncured adhesive as shown in Table 2. Most often a mixture of polyols is used to provide the desired performance. Aromatic isocyanates, such as methylene diphenylisocyanates (MDI), are generally used. Hydrogenated MDI is used to prevent yellowing of the adhesive when exposed to sunlight.

Type of Polyol	Characteristics
Polyesters (crystalline or amorphous)	The crystalline polyols can be used to give short open times and rapid green strength development but lower tack. Amorphous polyesters can improve adhesion to specific substrates and increase open time, if required.
Polyethers	Low Tg, amorphous liquids that help lengthen open and tack time, improve green strength, reduce viscosity and provide good low temperature flexibility.
Vinyl polymerized polyols	Typically high molecular weight glassy solids that can assist in building green strength and tack while maintaining extended open times.

Table 2: Types of Polyols Commonly Used in Reactive Hot Melt Polyurethane Adhesive Formulation^[1]

Moisture reactive polyurethane prepolymers have been combined with thermoplastic raw materials, such as ethylene vinyl acetate copolymers, styrenic block copolymer, polyolefins, and isobutylene / butyl rubber. This is another approach to formulating reactive hot melt adhesives with specific end-properties.

^[1] The compatibility and reactivity of all the materials must be considered to formulate storage stable products that are flowable at reasonable temperatures.

Other components used in formulating HMPUR adhesive include tackifier resins and waxes. Tackifiers are used to improve adhesion, improve high temperature resistance, and provide pressure sensitive characteristics. Usually C5-C9 hydrocarbons, polyterpenes and rosins are used. Waxes reduce the melt viscosity for easier pumpability and can help promote wetting on the substrate. Natural paraffin, microcrystalline wax, and polyethylene waxes have been used in HMPUR compounding.

Oils, plasticizers, fillers, pigments, antioxidants, ultraviolet stabilizers, and adhesion promoters are also used in compounding reactive hot melts similar to the way they employed in most conventional adhesive formulations. Flame retardancy is provided to HMPUR adhesives via fillers and other inert flame

retardant materials or, more effectively, by binding reactive flame retardant ingredients directly onto the polymer.^[2]

To choose the best raw materials for your polyurethane, use [TechDirect](#)



Curing and Processing Properties

Before the HMPUR adhesive reacts with ambient moisture, it must exhibit the properties of a conventional hot melt system. Typical application temperatures for HMPUR adhesives are in the range of 85-140° with melt viscosities from 2,000 to 80,000 cps. Application temperature and viscosity can be engineered by the balance of polyester and polyether components and the degree of amorphous structure in the polymer. Unless carefully formulated, HMPUR adhesives could exhibit poor viscosity stability due to their reactivity. This could lead to uncontrollable coating weights and variable performance.

New HMPUR systems can be applied at temperatures as low as 65°, depending on the substrate and type of equipment used.^[1] These lower viscosity systems are used in laminating and bonding to temperature sensitive substrates such as textiles. One of the distinct advantages of HMPUR systems is that they can be applied to temperature sensitive surfaces. In this way puckering, shrinkage, and/or destruction of delicate substrates (e.g., textiles) can be diminished or eliminated. In addition, energy consumption and the likelihood of employee burns are greatly diminished or eliminated.

Open time is defined as the time that the adhesive, once applied, remains in the molten state so that effective wetting occurs and adhesive bonds can be formed. The open times for HMPUR adhesives can be seconds to several minutes. As with most hot melt systems, the open time of the HMPUR is dependent, to a significant extent, on the thermal conductivity of the substrate being coated. The open times with high thermal conductivity substrates, such as metals, may be short. Substrates with relatively low thermal conductivity, such as wood, plastic laminates, and foams, could provide open times up to 5-10 minutes. Once the adhesive is applied and fully wets the substrate, the parts should be joined rapidly. Highly conductive substrates may gel the adhesive before it has a chance to fully wet the substrate resulting in poor adhesion. In these cases, a preheating of the substrate may be necessary for optimum adhesion.

Although HMPUR adhesives have good green strength, it should be noted that the initial strengths of conventional hot melt adhesives are generally greater than the initial strengths of HMPUR adhesives. As a result, the possibility of early stress (before full cure) should be carefully evaluated with HMPUR adhesive joints. The final strength and performance properties of the HMPUR adhesive is, of course, superior to conventional hot melt adhesives.

Once applied and gelled, a full cure typically occurs in one to four days depending on the temperature, availability of ambient moisture, and the specific formulation of the adhesive. The general difficulty with faster cure formulations is the possibility that they may prematurely cure in storage, within the applicator, or before the bond is made.

Generally, organometallic catalysts are used to accelerate cure of HMPUR adhesives as explained above. Without catalyst, the lap shear strength of HMPUR adhesive, bonding particleboard and metal sheet for example, usually remains below 100 psi (69 N/cm²) for several hours. However, catalyzed adhesives develop handling strength within 30 minutes (Figure 3). A proprietary catalyst developed by National Starch and Chemical is claimed to provide good melt stability with more consistent cure at different environmental humidities. This catalyst is capable of providing significant early lap shear strength, near 200 psi (138 N/cm²) in only 30 minutes.^[3]

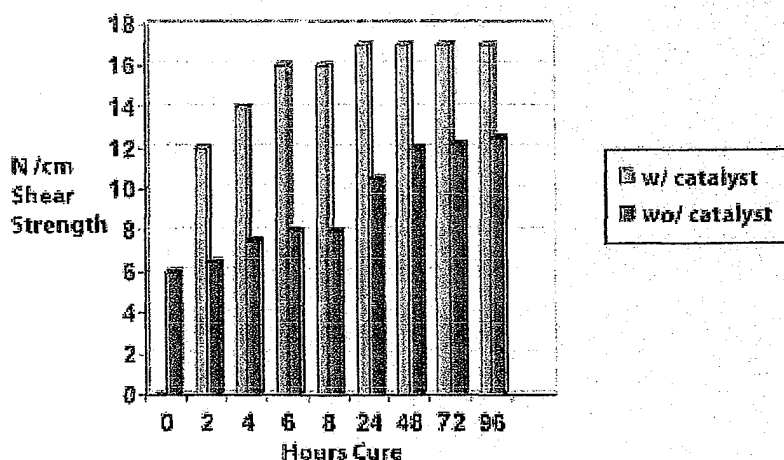


Figure 3: Strength development of HMPUR adhesives with and without catalyst^[8]

Green strength and open time can be built into a custom formulated HMPUR to meet specific needs and production requirements. In addition, the ability to independently control open time and green strength development generally will reduce or eliminate the effects of "memory" in the joint. The ability to control the open time allows the end-user to maximize productivity and reduce rejects or scrap.

Equipment Requirements



Compounding equipment for HMPUR adhesives generally requires both high shear and vacuum processing. High shear mixing is necessary to blend the polymers while vacuuming is required to remove moisture from the raw material. Low speed, high torque, high shear mixers are required to pull the solid rubber into the melt. Typically, the prepolymers are made in polyurethane prepolymer reactors. Most often the compounding is done in batch quantities; however, continuous processing equipment is available which eliminate the problem of clean-up between batches. The level of compounding complexity generally requires special equipment specifically designed for reactive polyurethane hot melts.

Applicators for HMPURs are also specially built for the adhesive and the application. One of the significant problems in market development of HMPURs over the years has been the lack of suitable, low cost delivery systems. HMPUR is commonly applied by extrusion. The moisture curing mechanism necessitates that the adhesive be isolated from ambient air except at the point of application. With moisture contamination prior to application, the adhesive can solidify within the mechanical confines of the applicator. Modern equipment designs have overcome the early complexity, unreliability, and high cost of early HMPUR applicators. Also the advent of cartridges and granular HMPUR adhesive forms has extended their use to more conventional equipment.

Minimal fixturing for HMPUR bonded joints is needed due to the controlled set time and rapid development of strength of the adhesive. Often a bonded assembly will develop sufficient strength and environmental resistance so that it can be moved to the next process (e.g., packaging, paint line, finishing) in a short amount of time.

Cleanup and purging had been an additional complexity and cost issue with early HMPUR systems. Generally, thermoplastic resins such as EVA are used to purge the HMPUR from the applicator by simple physical gravity. However, the advent of chemical purging agents has provided much greater purging efficiencies. Reactive purges are available that cap the reactive sites available on the uncured HMPUR polymer. By attaching themselves to these sites, the purge eliminates the polymer's ability to react with water. The entire mixture can then be easily pumped and removed from the applicator. The reactive purges are available in various solid hot melt forms that can be easily added to the extruder.



Applications

Good matches for HMPURs are applications that require high temperature resistance, fast production speeds, and the viscoelastic properties of an elastomer. Audio speaker cones, electronic enclosures, and the installation of sound dampeners are examples. The cured HMPUR adhesive can withstand temperatures from -40 to 100° for long periods of times and up to 125° for intermittent periods. HMPUR adhesives can be designed with widely varying properties for specific applications.

Reactive hot melt adhesives represent one of the fastest growing segments of the adhesive industry. HMPUR adhesives originally gained fame in the auto industry for assembling widely different substrates. Applications included instrument clusters, sound insulation, carpeting, seating, and decorative trim. With the advent of higher performance systems and systems that are easier to apply, these applications have been extended to exterior applications such as weather stripping, exterior trim, light lens units, and windshield assemblies.

Another fast growing market is the furniture industry. Here the fast production speeds and low VOC levels are the driving factors. HMPUR adhesives bond solid wood, wood composites, metal hardware, and decorative plastic laminates. They have also been used to bond thermoplastic films such as polyolefin or PVC. These adhesives are generally used in areas that see higher stress levels and high humidity, temperature, or chemical environments (e.g., baths, kitchens, and workshops). The manufacture and lamination of cabinets and countertops are also ideal applications for these adhesives. The ability to bond dissimilar substrates, metal hardware to wood cabinets for example, is a major advantage of HMPURs over conventional hot melts. Because of the short set times and rapid green strength development that are possible with HMPUR adhesives, profile wrapping is also a major growing application. This includes the wrapping of stiff profiling material, such as PVC extrusions or laminates, to the edges of products.

Another area where HMPURs are gaining a foothold is in the construction industry where the high temperature and moisture resistance of these adhesives are utilized. Examples are the assembly of door and window frames and corner covering for linoleum flooring. Mobil home and recreational vehicle manufacturers make extensive use because of their general usefulness on a variety of substrates and their processing speed.

The textile industry is also beginning to use significant quantities of HMPUR adhesives. Advantages in textile applications include:

- low viscosity behavior allowing for high line speeds,
- heat sensitive products can be rapidly coated and laminated,
- excellent moisture and solvent resistance allows for washing and dry cleaning,
- reactive flame retardant systems are available,
- capable of bonding low energy fabrics, such as porous Teflon and polyolefins.

Other Reactive Hot Melt Systems



There are several commercial reactive hot melt systems based on chemistry other than that of HMPUR. Certain reactive hot melt polymers (including polyurethanes) can be endcapped with organofunctional silanes. Organofunctional alkoxy silanes produce silane modified polyurethane prepolymers. The silane reacts with the unreacted isocyanate group on a typical prepolymer to form a urea linkage and terminal alkoxy silane groups. These groups then can react with moisture to form silane linkages between each prepolymer molecule and with the substrate. The advantage of this approach is the elimination of unreacted isocyanate and improved adhesion, especially to plastic surfaces.

Another type of reactive hot melt is based on acrylates that crosslink on exposure to ultraviolet (UV) light. [4,5] This adhesive includes free radical reactive double bonds and a photoinitiator in the adhesive formulation. These systems are generally used for pressure sensitive tape and label production. The UV curable acrylic resin is processed with standard hot melt equipment that can be used for SIS/SBS hot melts; the only special equipment necessary is the UV lamps for crosslinking. To coat the adhesive on a carrier, the adhesive has to be heated to 100-135°. In this temperature range the adhesive becomes liquid enough to be coatable with common slot or roll systems. Standard mercury, medium pressure UV bulbs, common to other UV applications, are typically used as the energy source.

Moisture curable silicone hot melt pressure sensitive adhesives are made from mixtures of silanol terminated silicone polymers and silanol functional silicone resin.^[6] These adhesives have light resistance, low surface energy, high temperature resistance, and the absence of solvents. They also have the advantages associated with reactive hot melt systems such as low application temperatures, low or no VOC, and single component application. These adhesives are made moisture curable through the introduction of hydrolyzable (Si-X) groups onto the polymer. Curable warm or hot applied silicone PSAs can provide high adhesion strength to low surface energy substrate, high temperature durability, and other performance features previously known for silicone and silicone pressure sensitive adhesive material.



Summary

The unique property that gives reactive hot melt adhesives their advantage compared to thermoplastic hot melts is that they cure to a thermoset material. Reactive hot melt adhesives offer the end-user many choices in formulation, application equipment, and applications. Rapid assembly time, unusually high bond strength, lack of VOCs, resistance to environmental extremes, and long life make these adhesives logical choices for an increasing number of demanding applications.

To get expert advice on the formulation of your Reactive Hot Melt Adhesives, contact us via [TechDirect](#)

References:

1. Chronister, M.A., "Heating Up", Adhesives Age, May 2001, pp. 34-40.
2. David, F.E. and Fromwiller, J.K., "Reactive Urethane Hot Melts for Textiles", Adhesives & Sealants Industry, March 1998, pp. 32-34.
3. Hung, J.M., "Fast Cure Reactive Hot Melt Adhesives Maintain Stability", Adhesives Age, February 1997, pp. 52-53.
4. Schumacher, K.H. and Sanborn, T., "UV-Curable Acrylic Hot Melts for PSAs", Adhesives & Sealants Industry, June / July 2001, pp. 42-44.
5. Endisch, S., et.al., "Warming Up to Mother Nature", Adhesives Age, August 2001, pp. 41-44.
6. Lower, L.D. and Jones, L.A., "Silicone Valley", Adhesives Age, February 2002, pp. 26-33.
7. Hubler, L, et.al., "Hot Melt Polyurethane Reactive Adhesives Targeted for Specific Applications", www.specialchem4adhesives.com, May 29, 2002.
8. Onusseit, H., "Numerous Processes Rely on Trends in Hot Melt Development", Adhesives & Sealants Industry, October / November 2002, pp. 28-34.

Close